

Instructions

1. The exam is for 75 min - an initial 15 min discussion period followed by 60 min writing period.
2. Writing is ONLY permitted during the second period.

Information you might find useful

Kinetic Theory of Gases

$$n(v) dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 dv; v_{mp} = \sqrt{\frac{2k_B T}{m}}; \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}; v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

Statistical Mechanics

$$q_{tr} = \sqrt{\frac{2\pi m k_B T}{h^2}}; q_{rot} = \sqrt{\frac{8\pi^2 I k_B T}{h^2}}; q_{vib} = \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} \approx \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}$$

Chemical Kinetics

$$\theta(b) = \pi - \int_{r_{min}}^{\infty} \frac{dr}{r \sqrt{\left\{ \left[1 - \frac{2V(r)}{\mu v^2} \right] r^2 - b^2 \right\}}}; \sigma_{AB} = 2\pi \int_{b_{min}}^{b_{max}} b db; \sigma_{AB,R} = 2\pi \int_0^{\infty} b P(b) db; k_f = \int_0^{\infty} f(v) v \sigma_{AB,R}(v) dv;$$

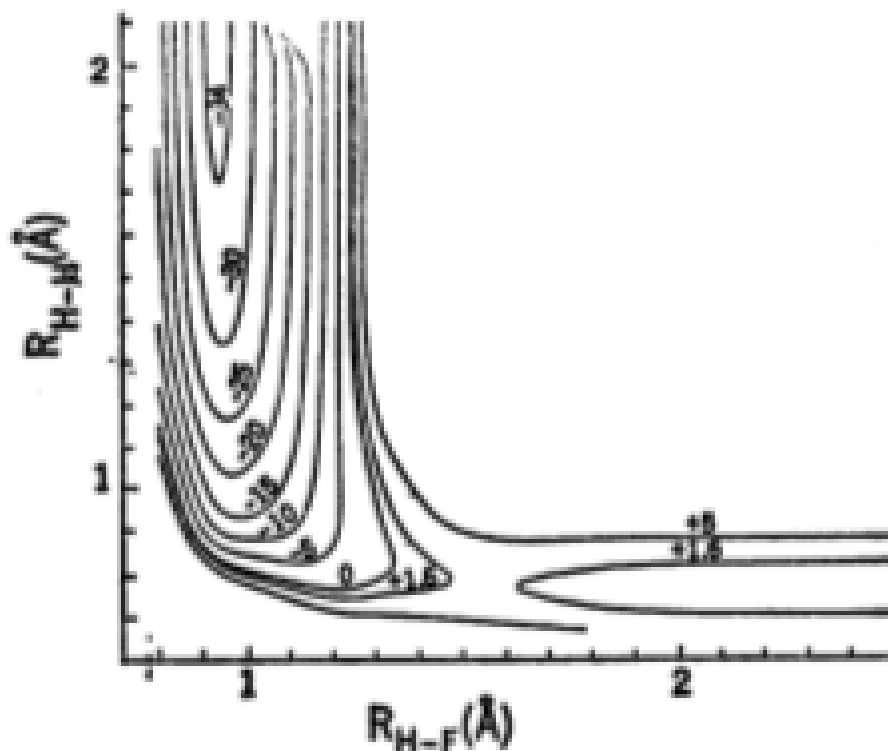
$$Z_{total} = N_A N_B 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^{\infty} \sigma_{AB}(v) v^3 \exp\left(-\frac{\mu v^2}{2k_B T}\right) dv; Z_{total} = N_A N_B (\pi \sigma_{AB}^2) \sqrt{\frac{8k_B T}{\pi \mu}}$$

Constants

$$h = 6.626 \times 10^{-34} \text{ J s}^{-1}; k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}; 1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$$

1. Obtain the reaction cross-section from the following data:

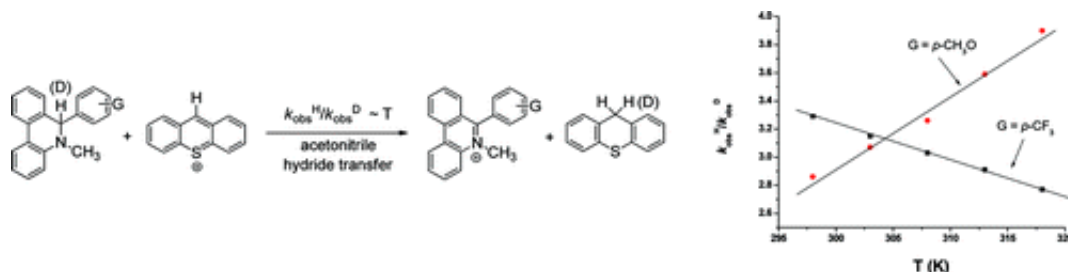
b (Å)	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
$P(b)$	0.84	0.83	0.85	0.78	0.80	0.75	0.80	0.83	0.72	0.21	0.10	0



The potential energy surface (PES) above is for collinear $F + H_2 \longrightarrow HF + H$. The next two questions relate to this PES.

2. What is the configuration of the transition state? Provide justification for your answer.

- Sketch the variation of the potential energy as a function of reaction coordinate (“reasonably to scale”) for the reaction. Energies are in kcal/mol in the figure.
- The figure below gives the temperature variation of k_H/k_D for hydride transfer reactions with two different substituents G. One of the lines represents “normal” variation and the other “anomalous.” Which of these lines represents “normal” variation of k_H/k_D with T ? Justify.



The next three questions relate to the Baldwin paper.

- Justify the use of the equation $72 \times \exp(-ka^2t) + 28 \times \exp(-kat)$ to model the data reported in Table 1.
- It is claimed that a least-squares fit of the data from Table 2 yielded $k = 1.16 \times 10^{-4} \text{ s}^{-1}$ and $k(d_4) = 0.99 \times 10^{-4} \text{ s}^{-1}$. Roughly estimate if these numbers are correct.
- “The substantial primary k_H/k_D effect anticipated for a rate determining [1,5] hydrogen shift converting 3 to 2 and 3- d_4 to 2- d_4 was not observed.” How “substantial” is substantial? Why is it expected to be substantial?

Hal Johnston, one of the most exceptional atmospheric chemists of the twentieth century, experimentally studied the reaction $\text{CF}_3 + \text{D-CD}_2\text{H} \longrightarrow \text{CF}_3\text{-D} + \text{CD}_2\text{H}$ and compared the rate constant with that from transition state theory.

- He claims that obtaining the rate constant for the full nine-atom activated complex is a tedious job, and hence constructed three simple models - five atom linear complex, four-atom linear complex, and a three-atom linear complex. If you were Johnston, what would be these simplified models? Sketch them.
- Set up (do not solve) the expression for the rate constant (in terms of the partition functions) in the three-atom linear model.
- What information would you need to obtain a numerical value for the rate constant with this model from transition state theory?